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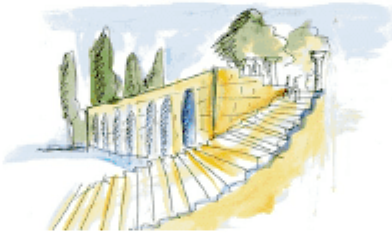

ORAL 32

DESTRUCTION OF DBP$_S$ AND THEIR PRECURSORS IN SWIMMING POOL WATER BY COMBINED UV-TREATMENT AND OZONATION

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Highlights

- UV treatment increased the reactivity of pool water to both chlorine and ozone
- Ozonation of UV-treated water decrease chlorine reactivity
- Genotoxic trichloronitromethane formed by ozonation was removed with UV treatment
- Continuous UV/ozone treatment decreases chlorine by-product formation
- Continuous UV/ozone treatment predicted to improve chlorinated pool water quality

Aims

The aim of the current study was to investigate the effect of a combined treatment system on DBP formation. As both ozone and chlorine preferably react with electrophilic groups in compounds [1], [2], we hypothesise that reactivity to chlorine, created by the UV treatment of dissolved organic matter in pool water, might also mean that there is increased reactivity to ozone and that ozonation might remove the chlorine reactivity created by UV treatment. Therefore, we first performed an experiment to range-find the effect of swimming pool water UV activation on chlorine reactivity. Second, an experiment was carried out to characterise the effect of adding various doses of ozone to pool water, with or without UV pre-treatment, before chlorination to study the effect on chlorine reactivity and the formation of chlorination by-products. Finally, the possible effect on chlorination by-product formation was investigated by a repeated, combined UV-ozone treatment interchanged with chlorination (repeated cycles of UV followed by ozone with subsequent chlorination). Toxicity estimation was used to evaluate water quality.

Methods

- UV treatment

Treatment was conducted using a quasi-collimated beam apparatus with a doped, medium pressure lamp (P = 700 W, ScanResearch, Denmark). To ensure constant spectra and emission output, the lamp was turned on half an hour before the experiment. Petri dishes (350 mL) were used as reaction vessels, while samples were maintained headspace-free and covered by a disc of quartz glass, to limit the volatilisation of the treated sample. To ensure homogeneity during irradiation, samples were mixed gently with a stirrer. The UV dose was determined according to a method described by Hansen et al. [3]. In summary, UV exposure in the collimated beam set-up was correlated to a real flow-through system on a pool, using the removal of combined chlorine. The UV system needs 1.0 kWh/m^3 to remove 90% of the combined chlorine. For the collimated beam set-up, required radiation time to remove 90% of the combined chlorine from the pool water was 12.3 mins.

- Ozonation

Ozonation was achieved by adding an amount of ozone stock solution to a water sample which resulted in maximum 10% dilution of the sample and the concentrations were back calculated according to actual dilution. Ozone dosage was determined by adding a sufficient amount of potassium indigotrisulfonate and a phosphate buffer to a separate ultra-pure water sample and measuring the absorbance of the unreacted indigotrisulfonate. A detailed description can be found in Hansen et al. [4].

- Chlorination

The formation of DBPs as a result of chlorination was investigated using a standardised DBP formation assay. The effect of chlorine concentration in the assay was also recently investigated by Hansen et al. [5]. In the current study, the same approach was used to simulate chlorination in the pool after the return of UV/ozone-treated water. Water samples were transferred to 40 mL glass vials after treatment in which chlorine and boric acid were added based on the chlorine consumption determined in pre-experimental tests. The aim was to have 1 ± 0.3 mg Cl_2/L after 24 hours at 25°C (measured by ABTS). Chlorination was performed in quintuplicate, with three samples used for DBP analysis and two for the determination of residual chlorine. Samples for DBP analyses were dosed with ammonium chloride solution (50 mg/L), to quench free chlorine which neither affects the already formed DBP [6] nor increases N-DBP formation [7]. The samples were analysed the same day.

Results

We found that UV treatment makes pool water highly reactive to ozone. The created reactivity towards chlorine decreases dose dependently with ozone dosage prior to contact with chlorine. Furthermore, the kinetics of ozone in UV treated pool water changed significantly from a half-life of 5 min to complete consumption in less than 2 min. Ozonation of UV treated pool water induced formation of some DBPs that are not commonly reported in pool water where trichloronitromethane is noteworthy for its genotoxic. However, this created genotoxicity was removed by UV treatments when repeated combined UV/ozone treatment interchanged with chlorination for 24h were conducted. The discovered reaction can form the basis for a new treatment method for swimming pools. The schematic of the proposed system has been shown in figure-1.

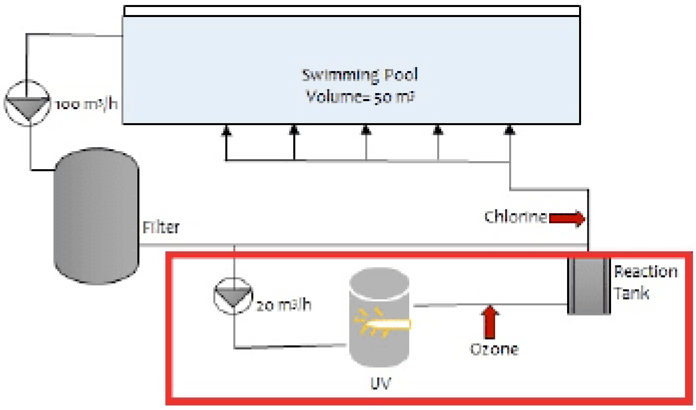

Figure 1: Schematic of proposed system

Conclusions

The treatment of swimming pool water by means of UV irradiation increased chlorine demand. Furthermore, the ozonation of pre-treated UV-irradiated pool water subsequently removed chlorine demand and decreased DBP formation. Combined treatment effectively reduced the level of disinfection by-products in pool water except for trichloronitromethane where an increase was observed. Trichloronitromethane was reduced after repeated treatment cycles and thus UV/ozone treatment is predicted to improve swimming pool water quality.

References

1. G. C. White, *Handbook of chlorination and alternative disinfectants*, vol. 3rd. New York: Van Nostrand Reinhold, 1992.

2. C. von Sonntag and U. von Gunten, *Chemistry of Ozone in Water and Wastewater Treatment: From Basic Principles to Applications*, 1st ed. IWA Publishing, 2012.
3. K. M. S. Hansen, R. Zortea, A. Piketty, S. R. Vega, and H. R. Andersen, "Photolytic removal of DBPs by medium pressure UV in swimming pool water.," *Sci. Total Environ.*, vol. 443, pp. 850–856, Jan. 2013.
4. K. M. S. Hansen, A. Spiliotopoulou, W. A. Cheema, and H. R. Andersen, "Effect of ozonation of swimming pool water on formation of volatile disinfection by-products - A laboratory study," *Chem. Eng. J.*, vol. 289, pp. 277–285, 2016.
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6. I. Kristiana, A. Lethorn, C. Joll, and A. Heitz, "To add or not to add: The use of quenching agents for the analysis of disinfection by-products in water samples," *Water Res.*, vol. 59, no. 0, pp. 90–98, 2014.
7. G. Hua, J. Kim, and D. A. Reckhow, "Disinfection byproduct formation from lignin precursors," *Water Res.*, vol. 63, pp. 285–295, 2014.

Combined UV-treatment followed by ozonation for the removal of by-product precursors in swimming pool water

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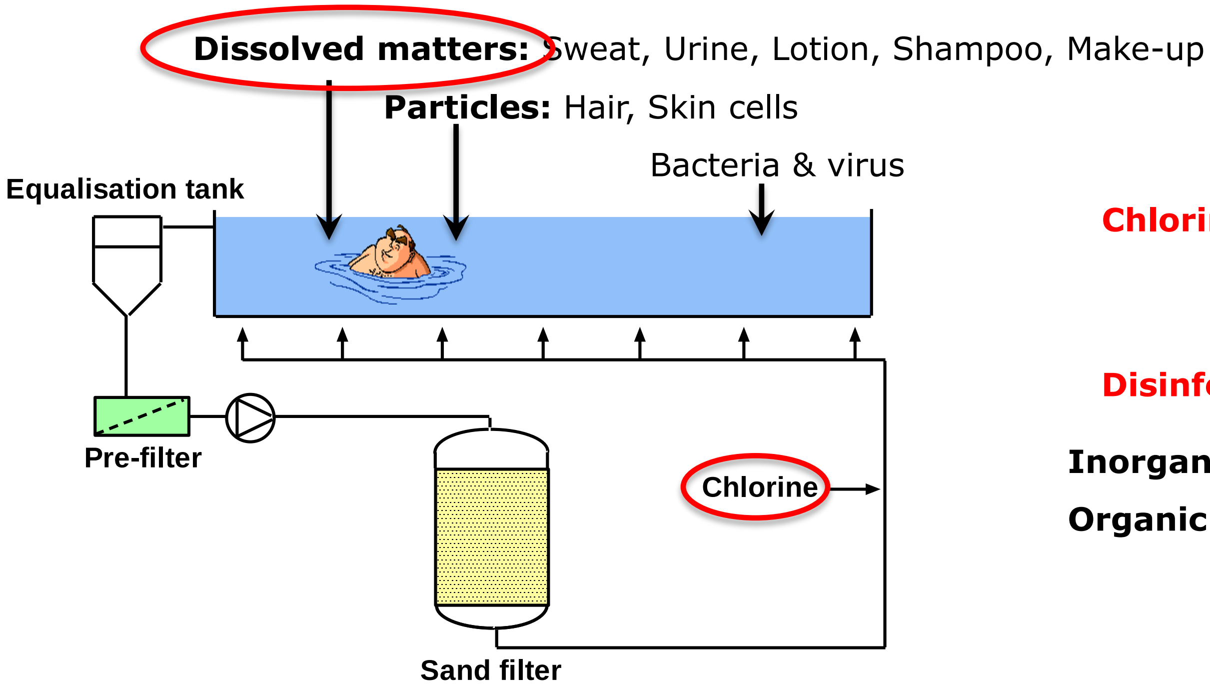
Kos Island, Greece

Swimming Pool
Disinfection By-Products



Chlorine + Dissolved Matter

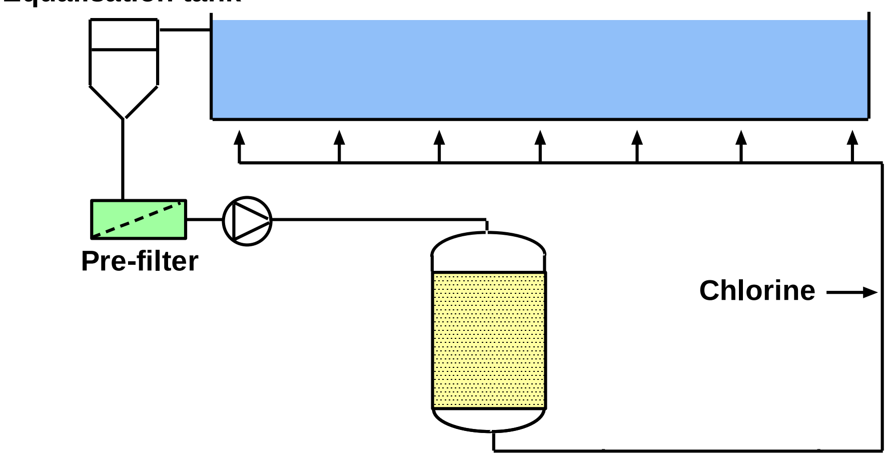
↓

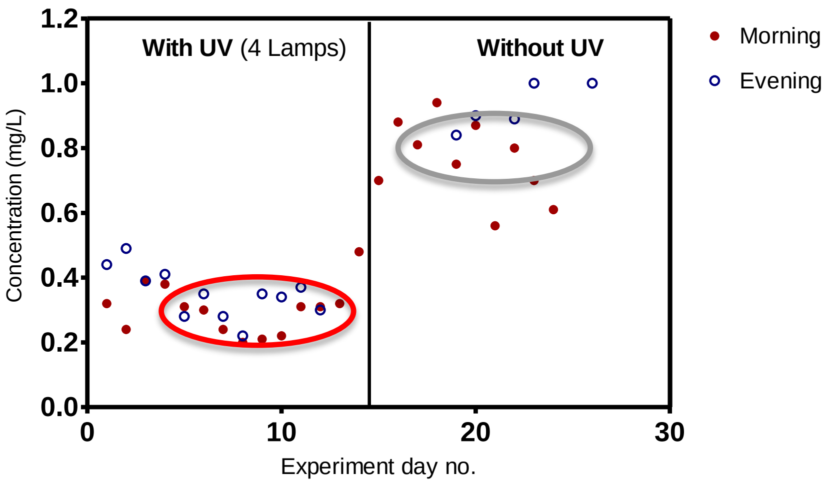
Disinfection By-Products (DBPs)

Inorganic e.g. Chloramines

Organic e.g. Trihalomethanes (THMs)
Haloacetonitriles (HANs)
Haloacetic acids (HAAs)

UV Treatment
Gladsaxe pool Copenhagen-Denmark

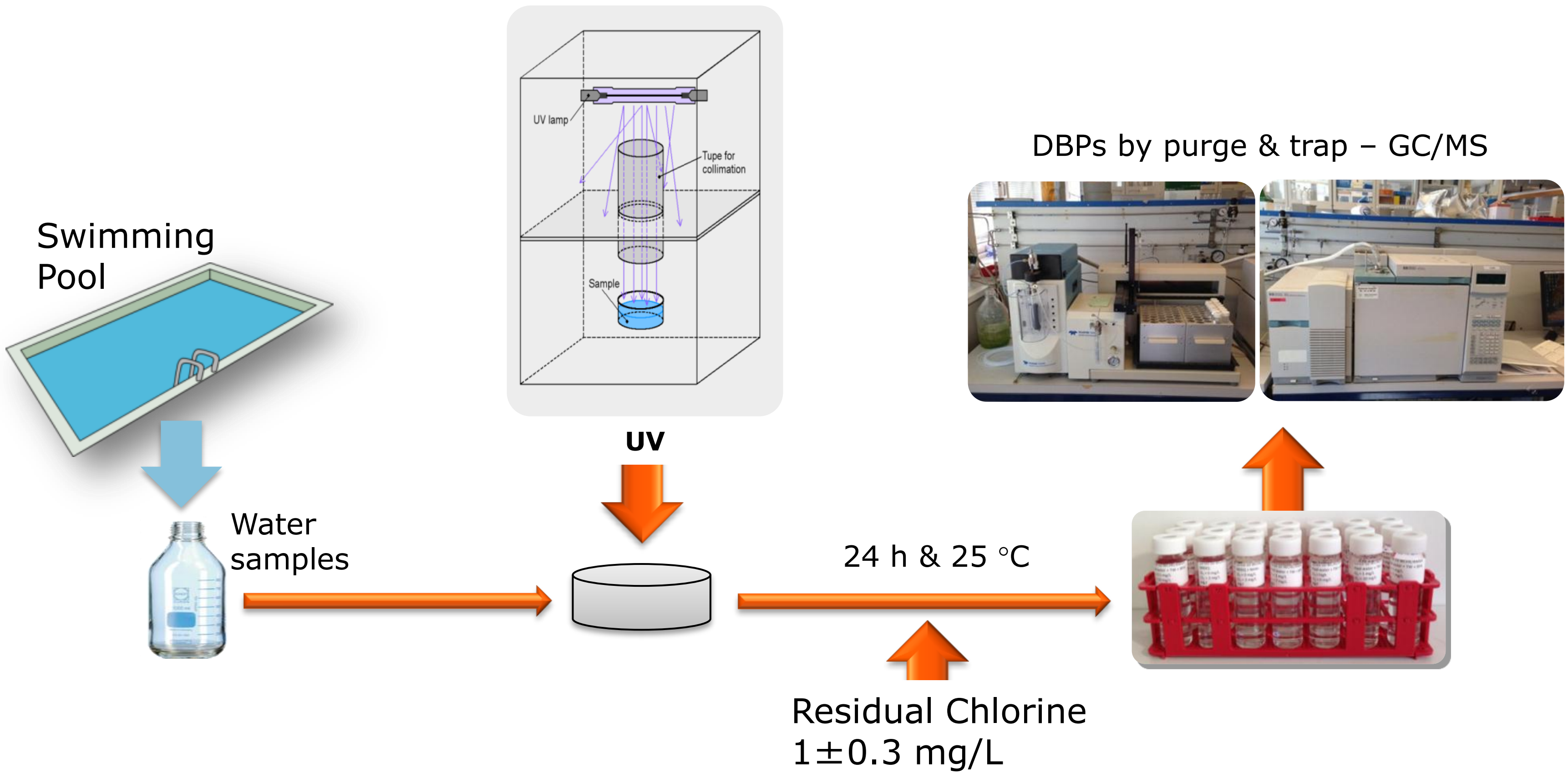




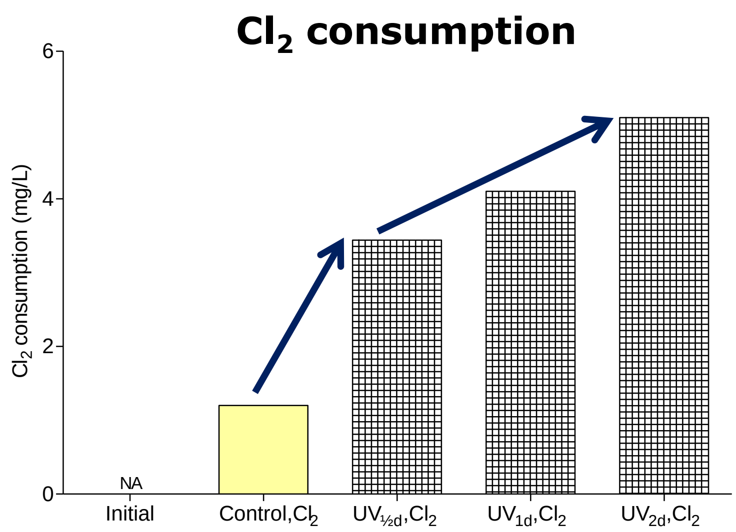
- UV treatment followed by Cl_2 → decreased combined Cl_2

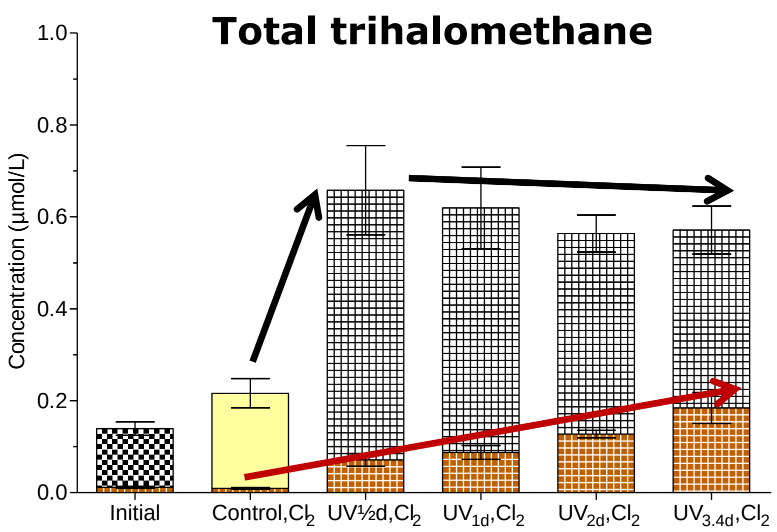
Kristensen et al., 2010, Report, Ministry of the Environment

UV Treatment
Experimental Setup



UV Treatment
Results

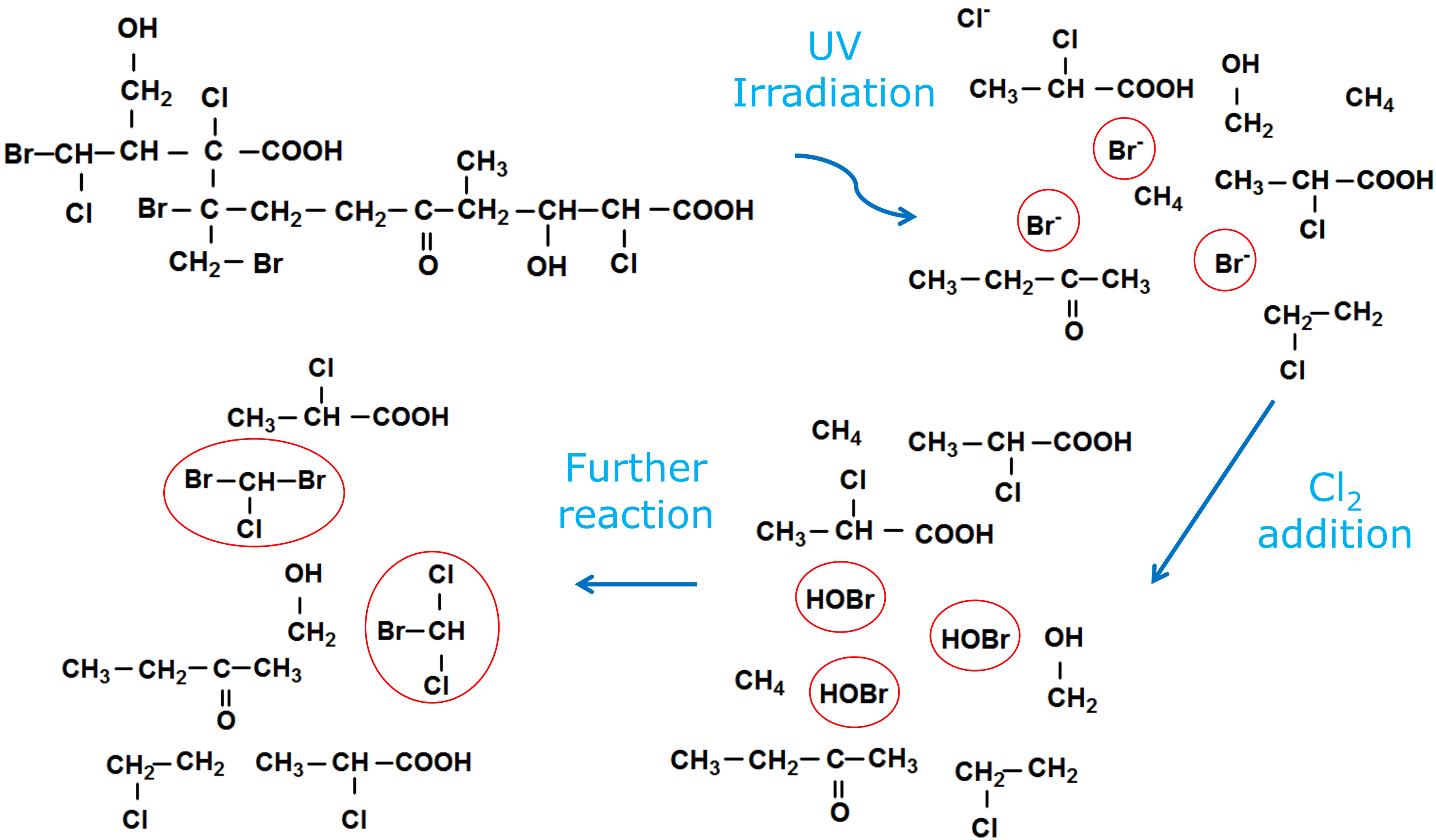




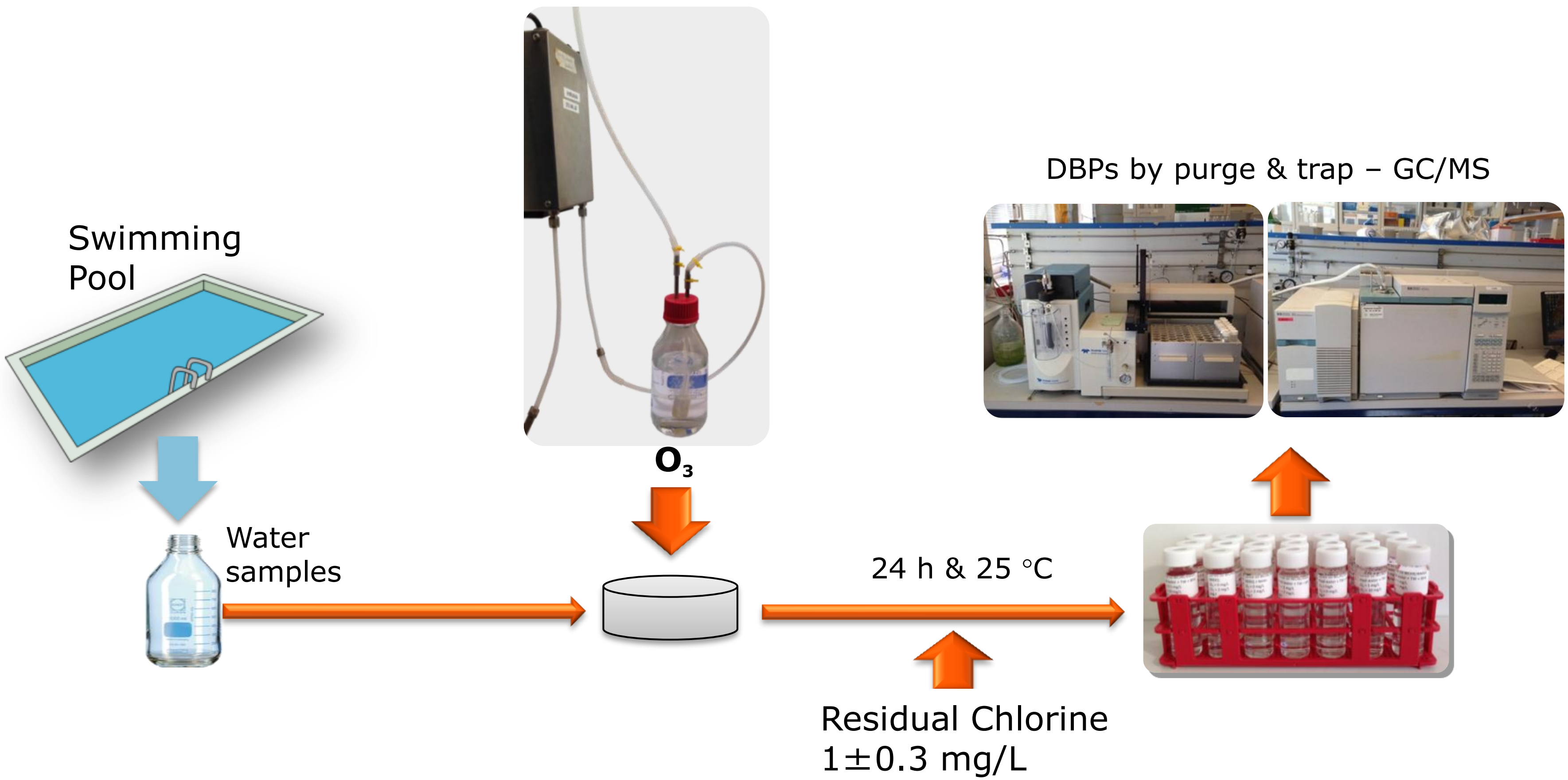
- UV treatment followed by Cl_2 → increased Cl_2 reactivity
- Increasing UV dose followed by Cl_2 → no effect on Total THMs
- Increasing UV dose followed by Cl_2 → increased Br-THMs

Spiliotopoulou et al., "Secondary formation of disinfection by-products by UV treatment of swimming pool water", STOTEN, 2015

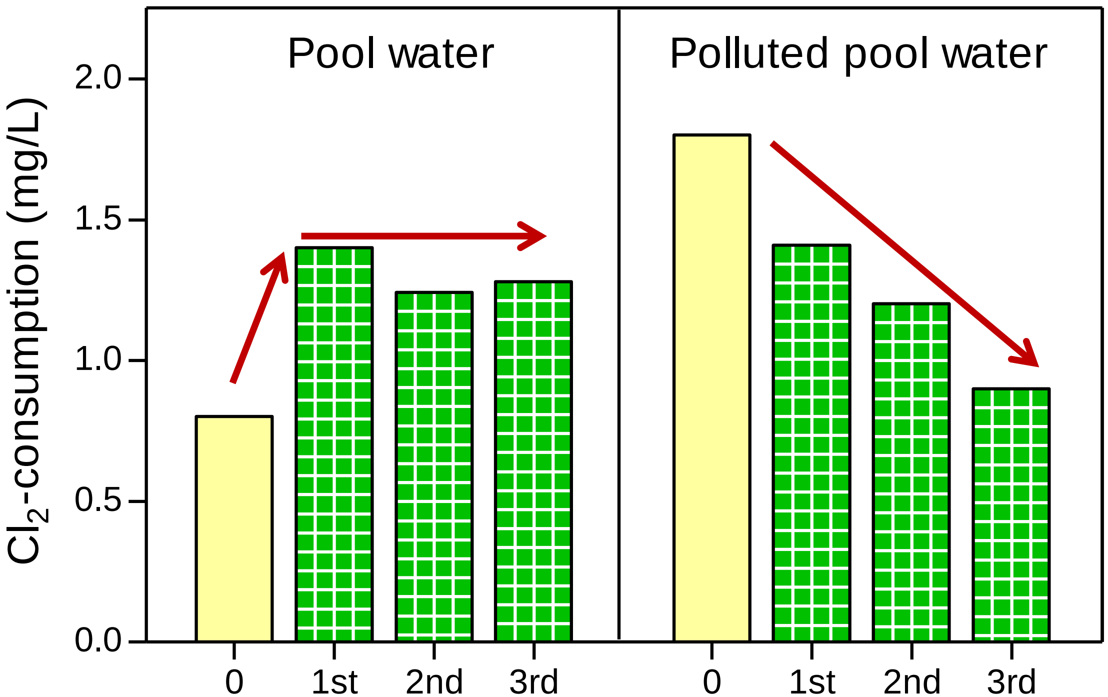
UV Treatment
Br-Cl-DBP Formation Theory

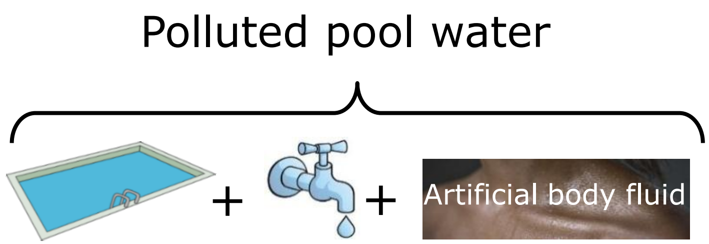


Ozonation
Experimental setup



Ozonation
Chlorine consumption



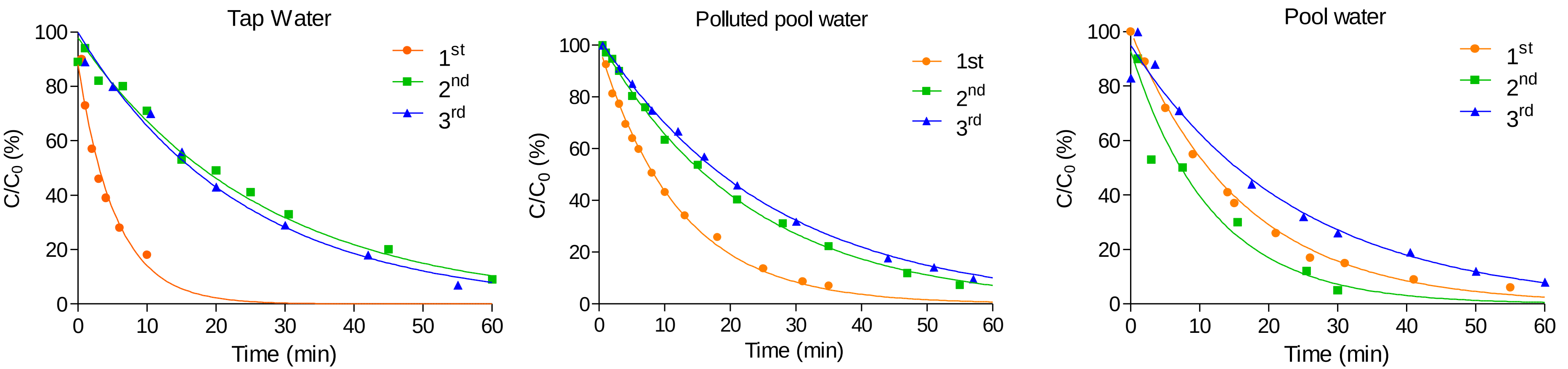


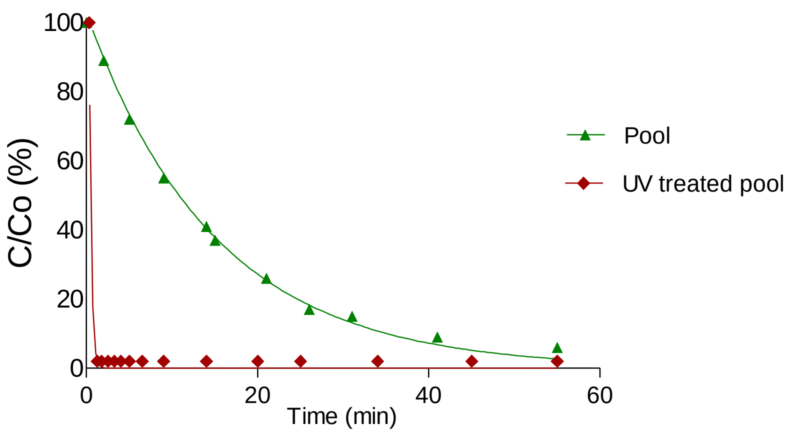
- Ozonation of pool water → increased Cl_2 reactivity
- Ozonation of polluted pool water → decreased Cl_2 reactivity

Hansen et al., Effect of ozonation of swimming pool water on formation of volatile disinfection disinfection by-products, Chemical Engineering Journal, (2016)

Ozonation

Ozone lifetime



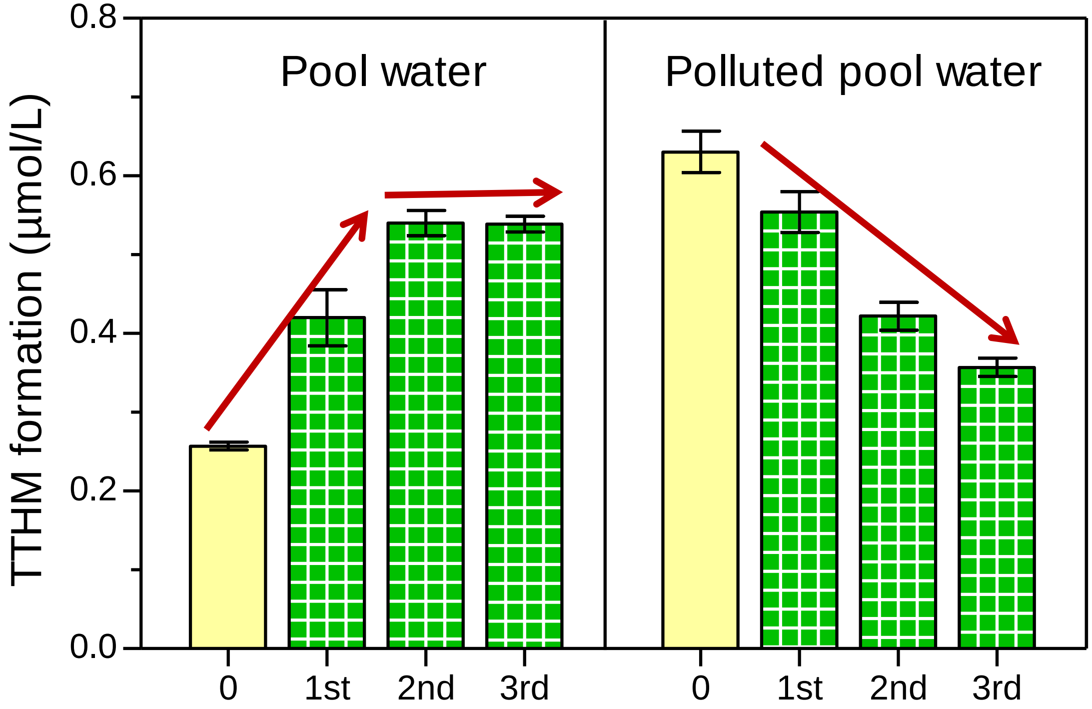


- Slow consumption of ozone
- Fast consumption of ozone

Reference

Cheema et al., 2017, Combined UV treatment and ozonation for the removal of by-product precursors precursors in swimming pool water, Water Research.

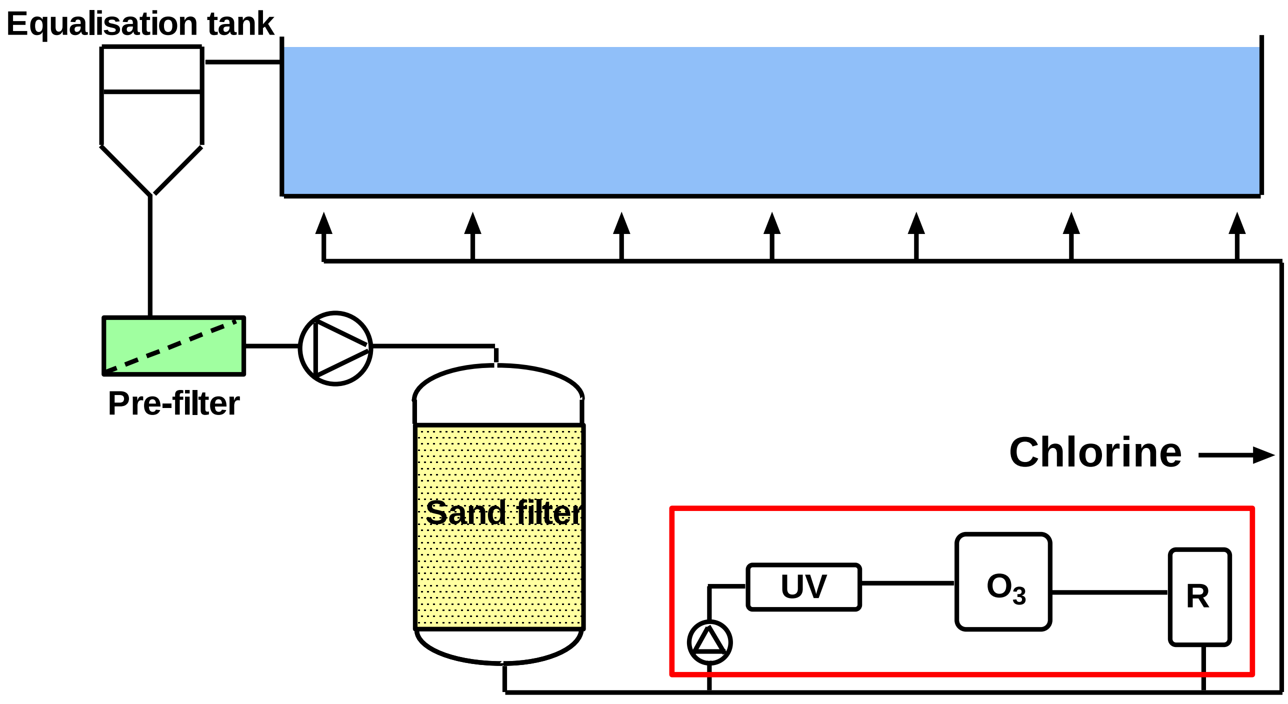
Ozonation
Formation of total trihalomethane



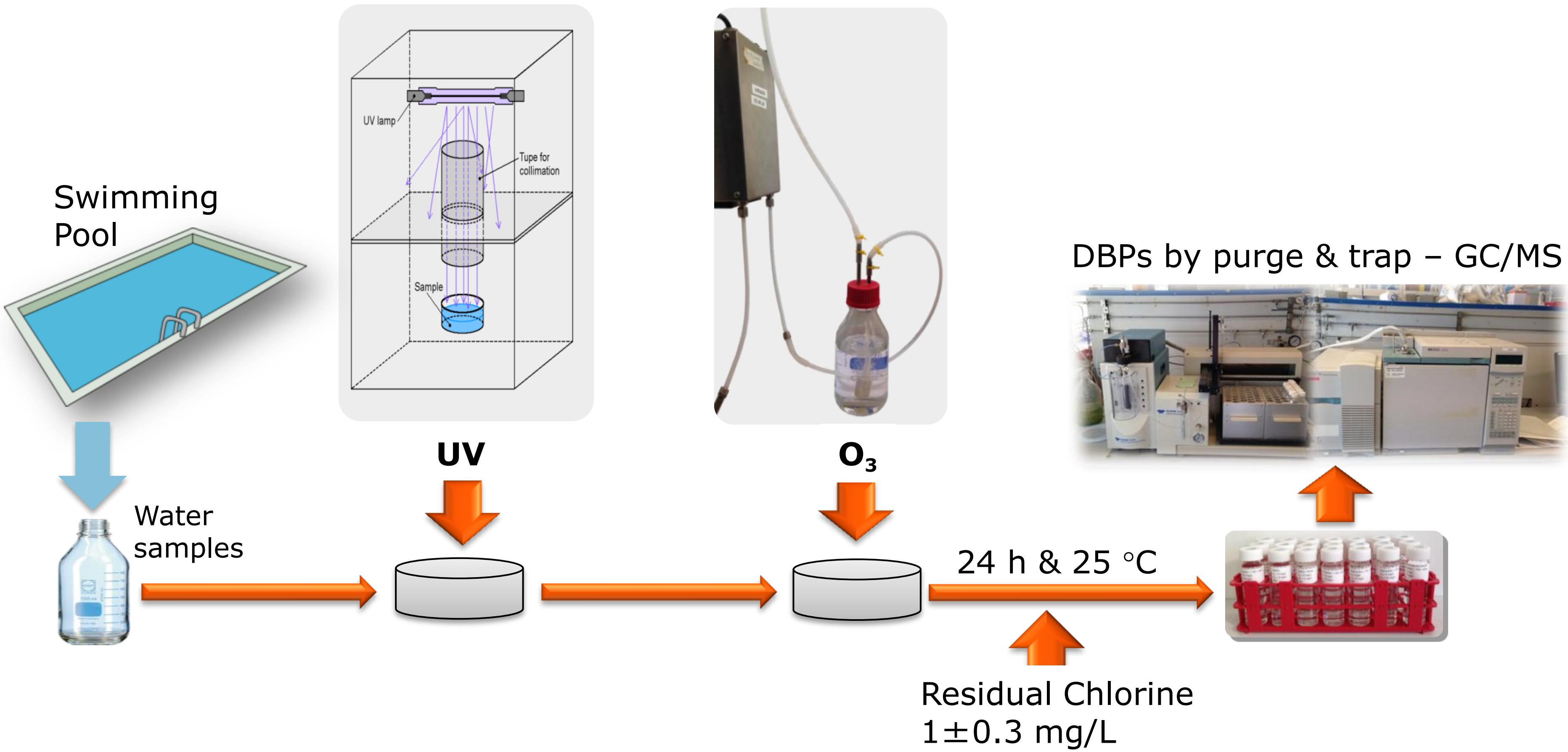
- Ozonation of pool water → increased THM
- Ozonation of polluted pool water → decreased THM

Hansen et al., Effect of ozonation of swimming pool water on formation of volatile disinfection disinfection by-products, Chemical Engineering Journal, (2016)

Swimming pools design
Proposed system

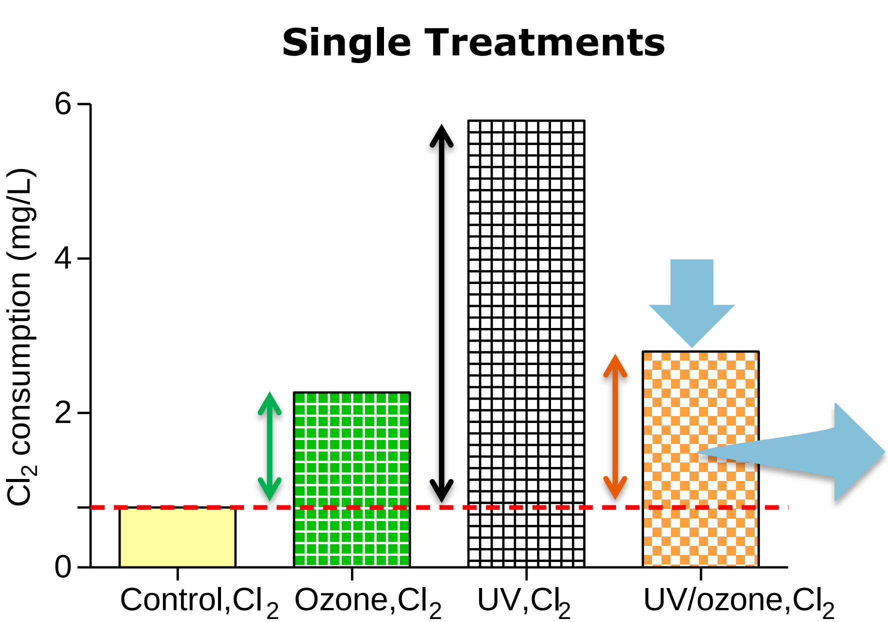


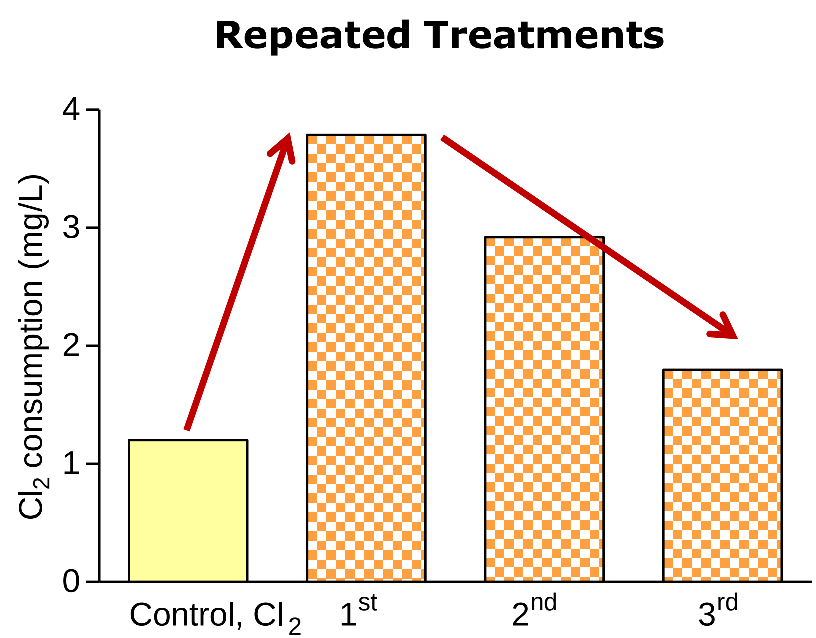
Combined Treatment (UV/O_3)
Experimental Setup



Combined Treatment (UV/O_3)

Cl_2 consumption

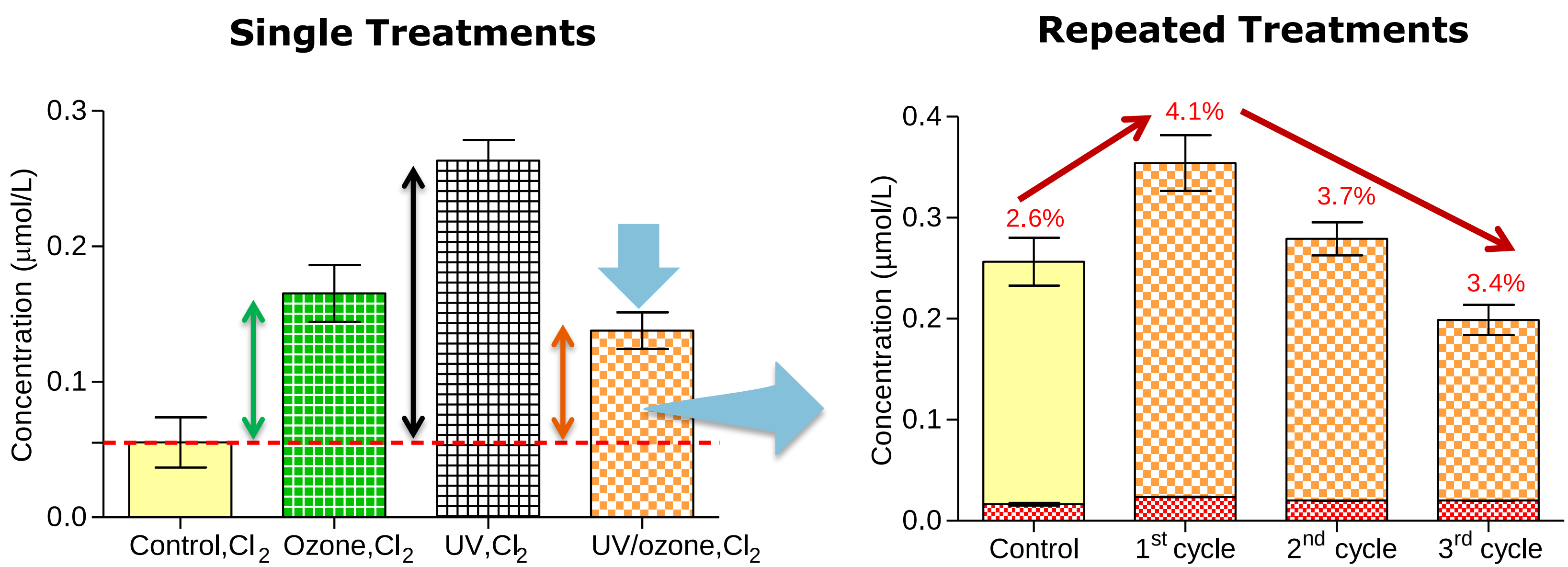




- Combined treatment followed by chlorination → increased Cl_2 reactivity
- Repeated combined treatments → decreased Cl_2 reactivity

Cheema et al., 2017, Combined UV treatment and ozonation for the removal of by-product precursors precursors in swimming pool water, Water Research.

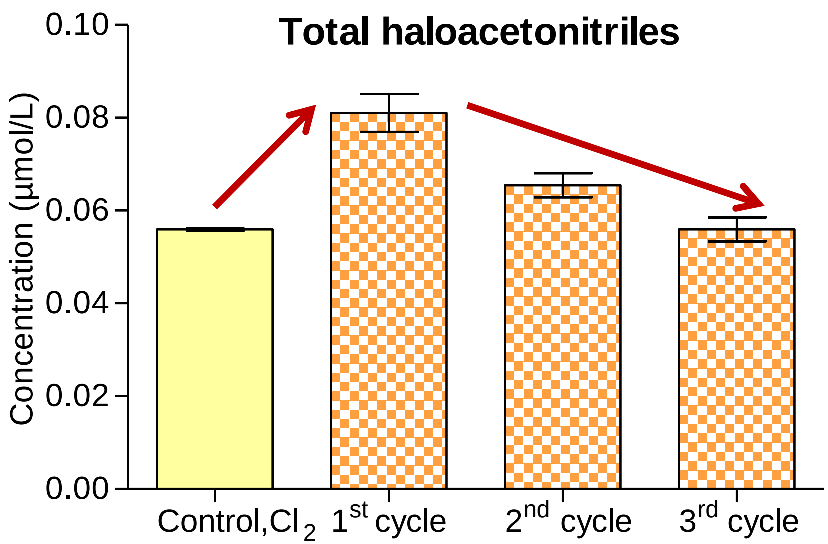
Combined Treatment (UV/O_3)
Total trihalomethane formation

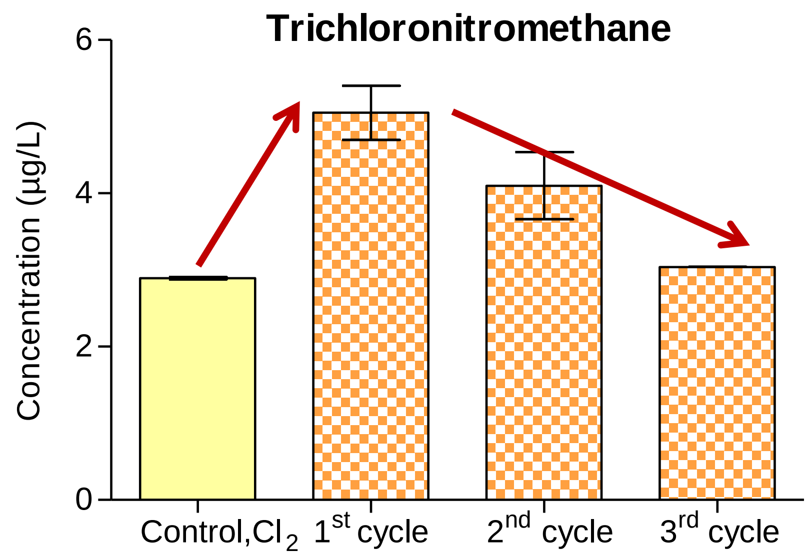


- Combined treatment followed by Cl_2 → increased THM
- Repeated combined treatments followed by Cl_2 → decreased THM

Cheema et al., 2017, Combined UV treatment and ozonation for the removal of by-product precursors precursors in swimming pool water, Water Research.

Combined Treatment (UV/O_3)
Total HANs & trichloronitromethane

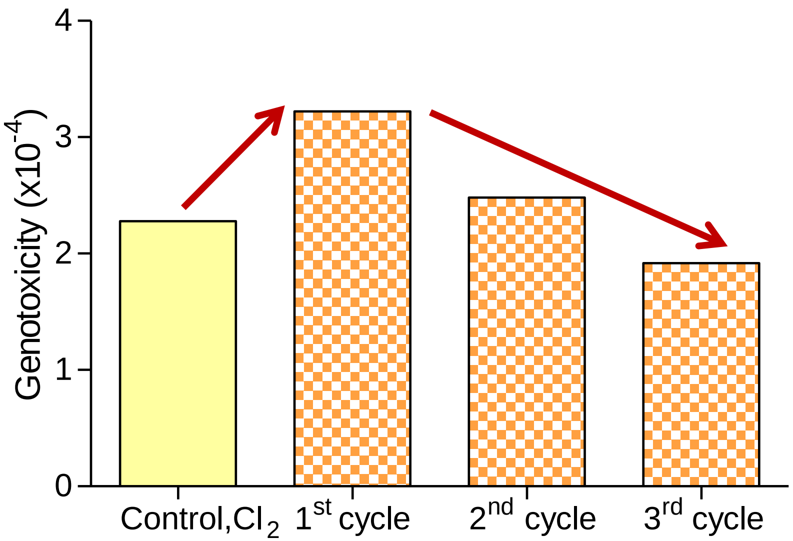




- Repeated (UV/O_3) treatment followed by Cl_2 → decreased Total HAN
- Repeated (UV/O_3) treatment followed by Cl_2 → decreased trichloronitromethane

Cheema et al., 2017, Combined UV treatment and ozonation for the removal of by-product precursors precursors in swimming pool water, Water Research.

Combined Treatment (UV/O_3)
Predicted toxicity



$$Toxicity = \sum \frac{C_i}{EC_{50,i}}$$

EC_{50} taken from Plewa et al. 2008

- The toxicity of the different groups
  Haloacetonitriles (HANs) > Haloacetic acids (HAAs) > Trihalomethanes (THMs)
- Repeated (UV/O_3) treatment followed by Cl_2 → decreased toxicity

Cheema et al., 2017, Combined UV treatment and ozonation for the removal of by-product precursors precursors in swimming pool water, Water Research.

Thanks for your attention!